RESULTS

Summary and Qualification of Data

In this report, data were summarized according to study (core or variability) and species (separate tables for each); the qualifier column was deleted for ease of mathematical manipulations (Appendix 1 – Tables A1 to A21). In these tables, any data point that was either non-detect (ND), below detection limit (BDL), or not analyzed (NA), was substituted with a "ND" to indicate that these data points were not used in this reports' data analyses. However, future analyses of these data sets may warrant use of values that were detected, but fell below the analytical detection limits (qualified by "BDL" in the QA/QC report). We therefore refer the reader to those results from each individual analysis, with associated analytical 'qualifier' columns, that appear in the QA/QC document as Appendices I and II.

The entire data set was merged into one (Table 13) where blank cells represent all qualified data points (those with ND, BDL, or NA qualifiers). In this table, PCB homologue group distributions were calculated. Because of the difficulties in accurately measuring the mono-substituted biphenyls, homologue distributions were calculated both with and without PCB congeners 1 and 3. In addition, Table 13 reports t-PCBs (reported as ng/g wet weight for biota and ng/g dry for sediments) as the sum of the concentrations of all PCBs that were detected above the BDL (as defined in the QA/QC report). Because PCBs are lipophilic chemicals, we also report t-PCB as a lipid-normalized concentration for biota (ng/g lipid).

Each whole fish PCB concentration value from the core studies was obtained from using the corresponding composite fillet and composite remains PCB values and calculating the (weight of fillet)/(weight of the whole fish) ratio and the (weight of remains)/(weight of whole fish) ratio (to determine the percent contribution from each). Values for white perch composited remains from the core study for two samples (Zone 2 fall and Zone 4 spring) were lost during analytical work-up. To estimate the corresponding whole concentrations for these two samples, values for composited remains were first calculated using the corresponding composited fillet values and an adjustment for lipid differences between fillet and remains. Once values for the remains were calculated, whole fish values were calculated using the weighted average technique describe above.

As mentioned in the QA/QC report, values for PCBs were not corrected for surrogate loss. However, in the case of the spring Zone 5 whole channel catfish, recovery of the surrogates was low. In order to compare these values to others having higher surrogate recoveries, values were transformed for this zone only to meet the average recovery of 90% observed in all samples (analyzed from Chesapeake Biological Laboratory). Justification for this lies in results from past studies in which surrogate correction for standard reference materials (SRMs) analyses having relatively low surrogate recoveries increased accuracy.

Fish Characteristics

White perch weights and ages ranged 27-220 g (mean ±s .d. = 95±43 g) and 2-9 years (4.4 ± 1.7 yr). Catfish weights and ages ranged 129-2170 g (676±404 g) and 3-19 years (8.1 ± 2.5 yrs). Within each species no weight or growth differences were detected due to the effect of zone, gender or season (ANOVA; $p>0.05$). Growth rates determined for white perch were similar to rates reported historically from the literature (Fig. 8). (Comparable growth data for catfish are unavailable in the published scientific literature). Condition (weight/length^3) did not vary significantly across zone, season, or gender for catfish. On the other hand, white perch collected in Zone 4 during Spring showed 3-fold higher condition index compared to white perch collected at other zones during spring or fall (ANCOVA; $p<0.001$).

Core Studies

Concentrations of t-PCBs (ng/g wet weight) for biota from all zones in fall and spring collections were variable (Figures 9 to 12). For example, concentrations ranged from 41 to 264 ng/g for invertebrates and 511 to 2,191 ng/g for channel catfish. Though concentrations were variable, some overall trends did surface. The following generalizations were based on inspection of concentrations that were not normalized for lipid content (ng/g wet weight):

- One average, across all zones, channel catfish had the highest concentrations, followed by white perch, small prey fish, and invertebrates (Figs. 9 and 10; 'grouped by species' plots).
- For fall collected samples, Zones 3 and 4 had the highest concentrations of PCBs within their biota; for spring collected samples, this trend was less pronounced as Zone 5 had elevated levels as well (Figs. 11 and 12; 'grouped by zone' plots).
- On average, concentrations were higher for spring collected biota than those captured in fall (Figs. 9 to 12).

It is widely accepted that when comparing accumulation of lipophilic contaminants such as PCBs, normalization to the lipid content is essential. For some data sets, trends observed from wet weight concentrations diminish or disappear when lipid content of biota is considered. By lipid normalizing concentrations of t-PCBs, variability between species and zones in both the fall and spring campaigns was again observed (Figs. 9 to 12). For example, invertebrate concentrations ranged from 4,344 to 26,001 ng/g lipid and a range of 10,577 to 22,582 ng/g lipid was observed for channel catfish. On average, lipid normalization did not reduce the variability in observed concentrations. The following generalizations were based on inspection of lipid-normalized concentrations (ng/g lipid basis):

- On average, fall collections of biota within Zones 3 and 4 had the highest lipid normalized concentrations; in the spring, Zone 5 collected white perch had the highest concentrations.
- Zones 2 and 5 had the lowest lipid normalized concentrations though this depended on the species and season.

- For fall collected prey fish and invertebrates from Zone 3, lipid-normalized concentrations were the highest in relation to all species; in spring, prey fish from Zone 3 had the highest concentrations.

By plotting lipid normalized t-PCB concentrations on a 3-D graph, the variability and trends among zones and species (described above) may be more easily visualized (Figs. 13 and 14).

Differences in surficial sediment concentration (ng/g dry weight) were observed though considerably less variability was observed compared to biotic phases within and between fall and spring collections. Average zonal surficial sediment concentrations ranged from 39 to 242 ng/g in the fall and from 28 to 200 ng/g in the spring. Highest t-PCB concentrations were observed in Zone 3 for both fall and spring campaigns, followed by Zone 4 (Fig. 15). Zone 5 had the lowest concentrations in both seasons. Upon normalizing concentrations to organic carbon content (ng/g OC), some variability among zones within a season decreased (Fig. 15). Highest concentrations were observed in Zones 3 and 4 in spring.

<u>Variability Studies</u>

For catfish, variability in fillet concentrations was assessed in three zones (Dredge Harbor (site 2CC), Tinicum Marsh (site 4CC) and just north of Pea Patch Island (5CC) (See Figs. 4, 5, and 7, respectively). Box plots of both fall and spring data for the three zones revealed tremendous variability in individual fillet concentrations (both wet weight and lipid normalized concentrations; Fig. 16). Individual t-PCB concentrations (both wet weight and lipid normalized concentrations) and the mathematical mean (and associated standard deviation) were compared to the fillet composite analyzed (Table 14 and Figs. 17 to 22). Overall, normalizing concentrations to lipid content did not reduce the variability in concentrations. However, in Zones 2 and 5, variability was reduced considerably except for one fillet in each of these zones. In all cases, the composite of fillets that were analyzed had similar values to the mathematical average of composites (Table 14). The relative standard deviation (expressed as a percent) of t-PCB concentrations from individual fillets (in ng/g wet weight) from each zone over the two seasons ranged from 24 to 80%. In four of the six variability studies, variability in concentrations (as denoted by relative standard deviation) increased upon lipid normalization.

Using log transformed wet weight concentrations of t-PCBs, there was a weak interaction of both age and zone on the individual fillet concentrations. ANOVA results also suggested a weak interaction between zone and lipid. However, the correlation between lipid and t-PCBs within a zone was not as usually predicted (increasing t-PCBs with increasing lipid content) because in Zone 4 there was an inverse relationship between lipid content and PCB concentration.

For white perch, variability in fillet concentrations was measured during three separate collections within Zone 5 during the fall. Again, box plots of the results of this study reveal tremendous variability (Fig. 23). Lipid normalizing the individual fillet concentrations did not significantly reduce the variability in these concentrations (Figs. 24 to 26). In variability study 1 from this zone, it actually increased the variability seen in concentrations. The mathematical mean of the individual concentrations were close to the analyzed concentration of the composite of the fillets. The relative standard deviation of t-PCB concentrations from individual fillets in the three regions within Zone 5 ranged from 60 to 90% on lipid normalized values (Table 14).

Calculation of BCFs, BSAFs and PPRs

Individual congener BCFs (bioconcentration factors) were calculated using the ratio of PCB content in tissue normalized to lipid, C_B, to the dissolved PCB concentration in the water, C_{WT}. The units for biota samples of mg/kg lipid divided by mg/L in water samples gives the BCF units of L/kg (Mackay and Fraser 2000).

BCF= C_B/C_{WD}

The BCF for total PCBs was calculated using the congeners common to the fish tissue and water analysis (Fig. 27).

Total BCF = $\sum$(congener specific C_B)/ $\sum$ (congener specific C_{WD})

Individual congener BSAFs (biota sediment accumulation factors) were calculated using the ratio of PCB content in tissue normalized to lipid, C_B, to the PCB concentration in sediment normalized to carbon, C_S, for biota samples.

BSAF= C_B/C_S

BSAF values were calculated for zones and using biota samples compared with their respective sediment sites for both seasons (Fig. 28).

Also known as trophic transfer factors, predator/prey ratios (PPR) are the ratio of lipid normalized PCB content in the predator to lipid normalized PCB content in the prey and may be used to address magnification. PPRs were calculated using:

PPR= $[PCB]_{predator}/[PCB]_{prey}$

Food web dynamics involve multiple dietary pathways with varying contributions, while simple predator/prey ratios address single species. Predator/prey ratios were calculated based on available prey items and knowledge of channel catfish and white perch diets (Fig. 29).

Principal Component Analysis of Congeneric Patterns

Though visual inspection of congeneric PCB patterns provides cursory insight into the differences in accumulation, PCA is helpful in reducing the complexity of the congeneric data set and further identifying differences in relative contribution of each congener. The first two principal components (PC1 and PC2) described 37% and 15% of the variability among the PCB congener patterns of all samples, respectively. That is, considering only the first and second principal components, 52% of the variance in congeneric patterns was captured. Using core (whole organism) congeneric data from both seasons, distinct separation and clustering of samples based on season, zone and species was observed (Fig. 30). Clustering of all perch samples occurred while remaining biota scattered. A notable sub-clustering occurred between spring and fall samples of all biota. Each fall core sample had a lower PC2 score than its respective spring counterpart. To factor out the separation due to season, principal component scores for fall and spring for each core sample were average and the PCA crossplot redrawn (Fig. 31). In this plot, separation or clustering among zones and species is more clearly seen. In the PC1 direction, samples were separated based on zone, while in the PC2, samples were separated based on species. Most striking is the difference in separation of perch from catfish, invertebrates and prey fish.

Clearly from these crossplots there are differences in the accumulated congeneric patterns between species and among zones. To pinpoint what congeners are most responsible for these pattern variations, coefficient weightings (or eigenvectors) were plotted (Fig. 32) for both PC1 and PC2. For PC1, changes in the distribution of the more heavily chlorinated congeners (octa-, nona-, and deca-substituted), especially congeners 206, 209, and coeluting congeners 208+195, were more responsible for driving the variations in patterns than other congeners. Though only 15% of the total variance is described by PC2, coefficient weightings suggest that it is primarily a small subset of congeners of varying degree of chlorination that are driving the differences in the PC2 direction.

Returning to the cross-plot with the added information from the eigenvectors, generalizations regarding pattern differences can be stated. White perch congeneric patterns were different from all other patterns (catfish, invertebrates, and prey fish). These differences are attributed to changes in both in the PC1 and PC2. Therefore, perch have, on average, a less ‘heavy’ pattern than catfish (especially from Zones 4 and 5) and invertebrates/prey fish from Zones 5. That is to say, they have a pattern that has a greater contribution from less chlorinated PCBs. The cross-plot also provides interesting information regarding zonal differences in patterns among each biotic group. It is clear that as the collection zones go from up-river (Zone 2) to down-river (Zone 5), patterns within each species adopt a more “heavy” (more chlorinated) congener distribution.

Though PCA allows much congeneric data to be reduced and more easily assessed, calculating the distribution of congeners based on homologue groups also provides some insight into pattern differences and similarities between species and zones. Homologue distributions for each species in each season were calculated (Figs. 33 to 36). Again, the overall patterns that were observed through PCA can be seen through comparison of homologue patterns. Noteworthy is the shift to “heavier” patterns from Zone 2 to Zone 5. The larger relative contribution from octa-, nona-, and deca-chlorobiphenyls in catfish, invertebrates and prey fish from Zone 5 is evident. This pattern shift is mirrored in the sediment distributions (Fig. 37).

In assessing the differences in congener distributions, it was apparent that both congeners 206 and 209 were present at relatively high levels in Zone 4 and particularly Zone 5. However, this shift was more evident in catfish, sediment, prey fish and invertebrates, rather than with white perch (Fig. 38). For the fall collection, white perch concentrations of congener 209 remained relatively low and invariant while in the spring they increased (Figure 39) though magnitude wise were less than those for catfish. For catfish, lipid normalized concentrations increased with distance down-river, except in the spring where concentrations in Zone 4 were highest.